

# Atomic scale coexistence of periodic and quasiperiodic order in a 2-fold Al-Ni-Co decagonal quasicrystal surface

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*Decagonal quasicrystals are made of pairs of atomic planes with pentagonal symmetry periodically stacked along a 10-fold axis. We have investigated the atomic structure of the 2-fold surface of a decagonal Al-Ni-Co quasicrystal using scanning tunneling microscopy (STM). The surface consists of terraces separated by steps of heights 1.9, 4.7, 7.8, and 12.6 Å containing rows of atoms parallel to the 10-fold direction with an internal periodicity of 4Å. The rows are arranged aperiodically, with separations that follow a Fibonacci sequence and inflation symmetry. The results indicate that the surfaces are preferentially Al-terminated and in general agreement with bulk models.*

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Unraveling the relationship between atomic structure and physical properties drives much of physics and materials science. Quasicrystals provide a special challenge because their atomic structure—well-ordered but not periodic [1]—is clearly associated with an array of unusual mechanical [2,3] and electronic [4] properties. While most known quasicrystals are icosahedral, with quasiperiodic bulk structure in all three dimensions, the decagonal quasicrystals have a structure that is periodic in one dimension and quasiperiodic in two.[5] They possess a 10-fold symmetry axis along the periodic direction, and two sets of five equivalent 2-fold symmetry axes rotated by  $36^\circ$  in the quasiperiodic plane. The 2-fold surfaces thus provide, within the same surface, a periodic direction along the 10-fold axis, and an aperiodic direction perpendicular to it. Surface properties that might depend on the existence of periodicity, such as friction, can thus be uniquely studied [3].

In this paper, we present a microscopy study of such a surface to unravel its atomic structure. We show that, as predicted from the bulk, it contains both periodic and aperiodic atomic arrangements that, together with a characteristic step-terrace structure, indicate that it exposes the Al-rich planes of the bulk.

The bulk structure of decagonal quasicrystals has been studied by high-resolution transmission electron microscopy and x-ray and electron diffraction [5]. These studies show that it consists of ordered arrangements of columnar clusters with pentagonal symmetry and diameter of 20 Å. The 10-fold surface of the Al–Ni–Co decagonal quasicrystal—the surface that is quasicrystalline in both dimensions--has been studied by low energy electron diffraction (LEED), ion scattering spectroscopy and scanning tunneling microscopy (STM) [6-10], but there are still important issues, such as atomic structure and composition, that remain controversial [8,9]. Some authors have attributed sites of high tunneling probability in the STM images to transition metal atoms [8], while others have identified these sites as Al atoms.[7,9] A further point of discussion is whether the surface termination is enriched in Al relative to the bulk composition [6,7]. In contrast to the 10-fold surface however, only a few studies of the 2-fold surface [6, 11,12] have been reported.

The experiments were performed in an ultrahigh vacuum chamber (base pressure in the  $10^{-10}$  Torr range) equipped with LEED, Auger electron spectroscopy, and an AFM/STM head from RHK [13]. Samples and cantilevers were transferred from air through a load-lock. Two types of conductive cantilevers were used, coated with approximately 30 nm of either  $W_2C$  or TiN, with spring constant of 48 or 90 N/m [14]. The high stiffness of the cantilevers suppressed the jump to contact instability and ensured stable tunneling.

Single grain decagonal  $\text{Al}_{72}\text{Ni}_{11}\text{Co}_{17}$  quasicrystals were grown at the Ames Laboratory in Iowa State University, and cut and polished to expose the (10000) surface [15]. In the UHV chamber they were cleaned by cycles of  $\text{Ar}^+$  sputtering at 1 keV, and annealed for 1 to 2 hours by electron bombardment at a temperature between 1100 K and 1200K, as monitored by an optical pyrometer.[13,16] As reported by Cox et al. the surface morphology is critically dependent on annealing temperature [10]. We found indeed that the surface undergoes a phase transformation above 1200K.

Figure 1(a) shows an STM image of the surface at  $V_s = +1.0\text{V}$ ,  $I_t = 0.1\text{nA}$ . Terraces separated by several types of atomic steps are visible. From the line profile (Fig. 1b), the heights of the steps are  $1.9 \pm 0.1 \text{ \AA}$ ,  $4.7 \pm 0.1 \text{ \AA}$  (short,  $S_H$ ), and  $7.8 \pm 0.2 \text{ \AA}$  (long,  $L_H$ ). We also observed steps of  $12.6 \pm 0.3 \text{ \AA}$  height ( $S_H + L_H$ ). Given the lack of periodicity, the existence of steps with such peculiar heights is a clear indication that particular atomic terminations, aluminum as we will show later, are selected because of their thermodynamic stability. The ratios between the  $S_H$ ,  $L_H$ , and  $L_H + S_H$  distances satisfy the Golden Mean ( $\tau \sim 1.618$ ), reflecting the aperiodic structure along the [10000] direction.

The terraces separated by  $S_H$ ,  $L_H$ , or  $L_H + S_H$  height steps contain rows of atoms with internal  $4.0 \pm 0.2 \text{ \AA}$  periodicity (fig. 2), while in the terraces next to the  $2 \text{ \AA}$  steps the rows have  $8.0 \pm 0.3 \text{ \AA}$  periodicity, double that in the other terraces [17]. These smaller steps had not been reported before. The STM observations agree with the LEED pattern, which consists of sharp spots corresponding to  $4 \text{ \AA}$  periodicity along the 10-fold axis, and streaks reflecting  $8 \text{ \AA}$  periodicity in smaller domains, in agreement also with the observations of Theis et al. [11]. Only 10-20% of the surface shows rows of  $8 \text{ \AA}$  periodicity in domains that are relatively small ( $< 100 \text{ \AA}$  as shown in Fig. 1). This is consistent with the elongated spots observed in the LEED pattern. In the bulk, planes located  $2 \text{ \AA}$  below pure Al planes have compositions that include Ni and Co (see below), which are of higher surface energy.

Figure 2(a) shows a collage of two high resolution STM images of a terrace. Except for a defect in the form of a missing row (visible as a dark band), it consists of atomic rows of close, but not exactly the same, apparent height, with variations of  $\pm 0.3 \text{ \AA}$ . Two different lengths,  $S = 7.7 \pm 0.3 \text{ \AA}$  and  $L = 12.5 \pm 0.4 \text{ \AA}$ , separate the rows and define the sides of pseudo unit cells. Secondary rows of lower apparent height are visible inside the cells, two within  $L$  and one within  $S$ , as shown in Fig. 2(b). The spacing between these secondary rows are  $L_2 = 4.9 \pm 0.3 \text{ \AA}$ , and  $S_2 = 2.8 \pm 0.2 \text{ \AA}$ . As shown in the figure, an intermediate-level partition can be considered with  $L_1$  and

S<sub>1</sub> separations, where L<sub>1</sub> = L<sub>2</sub> + S<sub>2</sub> and S<sub>1</sub> = L<sub>2</sub>. The ratios L/S, L<sub>1</sub>/S<sub>1</sub> or L<sub>2</sub>/S<sub>2</sub> are all close to the Golden Mean.

[illegible]

A few other STM studies of aperiodic surfaces with spacings following Fibonacci sequences have been reported. Cai et al. found that lines can be drawn through the 5-fold motifs of Al-Cu-Fe five-fold surfaces such that the distances satisfy part of a Fibonacci sequence [18]. Ledieu et al. reported pseudomorphic Cu overlayers on the Al-Pd-Mn icosahedral surface with two different separations between Cu rows [19], also following part of a Fibonacci sequence. As far as we know, our results are the first surface observation of *inflation symmetry* for atomic rows whose sequence follows a Fibonacci sequence. In contrast to our observations, the atomic structure of a 2-fold Al-Ni-Co surface reported by Kishida et al. did not show quasiperiodic ordering or evidence of the Fibonacci sequence along the 2-fold direction.[6] We suppose that this is due to the relatively high temperature treatment performed by these authors. According to our observations this changes the structure of the surface into a new phase, probably due to preferential evaporation of Al. Additional information is provided by images acquired at different polarities. Since the tunneling current depends on the local density of states, it provides information on the electronic character of the surface. Figure 3(a) and 3(b) show STM empty and filled states images of the same area. The profiles across the rows, shown in Fig. 3c, indicate that the contrast depends on the polarity and that there are three types of electronically different rows, denoted A, B, and C. Type A rows have the highest contrast in the empty state images (marked by lines in Fig. 2c), and lowest in the filled state images. Type B rows have opposite contrast behavior, i.e., low in empty state images, and high in filled state images. Type C rows are separated from A and B by an  $L_2$  segment and have relatively constant contrast in both polarities.

With this information we can proceed to examine proposed structural models based on bulk x-ray diffraction.[5] We examined three models.[8,20,21,22]

First we consider the model of Deloudi et al. [21] for the Co-rich phase of decagonal Al-Co-Ni. This model is based on a novel columnar cluster with 20 Å diameter extracted from the W-approximant,  $\text{Al}_{72.5}\text{Co}_{20}\text{Ni}_{7.5}$ . This model proposes 8 Å periodicity, inconsistent with the 4 Å periodicity found in our STM results.

The second model, due to Cervellino et al. [8, 22] is for Ni-rich phase of Al-Ni-Co. Although the 4 Å periodicity is present in this model, the observed L and S sequence, as well as that of the daughter segments  $L_2$  and  $S_2$ , are not predicted by the model.

Hence, we conclude that the best match (but not perfect as we shall see) is with the model of Takakura et al. [20] for  $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$ . First, its interlayer periodicity matches the 4 Å observed in the STM images. Second, among the many possible planes that can be generated by cuts parallel to the 2-fold plane, the planes made of pure Al are the only ones that: (a) contain rows with spacings matching the observed L and S sequences and also the daughter segments  $L_2$  and  $S_2$ , including the inversion discussed above, as shown in Fig. 4(a); (b) contain three compositionally different rows that can match the polarity dependent types A, B and C observed in the STM images; (c) are separated by distances that match the observed step heights  $S_H$  and  $L_H$ ; and (d) are separated by 2 Å from a plane containing transition metals (Co, Ni) that might correspond to the 2 Å terraces.

The Al termination (Fig. 4b) is presumably driven by the lower surface energy of Al relative to the two transition metals, consistent with the observation that icosahedral quasicrystals exhibit Al-rich terminations, selected from among the possible bulk layers.[23]

Fig. 4(c) shows that the positions of the topmost Al atoms in that surface map directly onto the positions of high tunneling probability in the STM image. These positions do not depend upon bias voltage, although their relative intensities do, as in Fig. 3. Hence, the “bumps” in the STM image represent Al atoms on the 2-fold surface.

The agreement with the Takakura model, however, is not perfect. The model exhibits local mirror symmetry planes, shown by the broken line arrows in Fig. 4(a). This symmetry is lost by the different contrast of the Al atoms (Fig. 4c), which varies with bias voltage. Even the partially good agreement with the model is remarkable however, because of the large number of structural details that can be explained with it. Nonetheless, the exceptions to the agreement should not be minimized. Another is the fact that the model is for the Ni rich alloy (Ni:Co =20:8), which has 4 Å periodicity, while the nominal composition of our alloy is Ni:Co =11:17, which borders on a phase with 8 Å periodicity at low temperature [5]. However, our sample could be quenched in from the 5fHT state, which is a high-temperature basic Co-rich phase with 4 Å periodicity [24]

Since both HT Co-rich and Ni-rich decagonal phases correspond to pentagonal tilings and have 4 Å period, the Takakura model could provide a reasonable structural interpretation.

In conclusion, we have shown that the atomic structure of the 2-fold, (10000) surface of Al-Ni-Co mainly consists of atomic rows of atoms with 4 Å periodicity along the 10-fold direction and aperiodically spaced in the 2-fold direction. They occupy terraces spaced by the same distances that separate the Al planes in the bulk. The rows are separated by short and long distances in a Fibonacci sequence. Nested daughter rows are present that extend the sequence (inflation symmetry), confirming quasicrystallinity in the aperiodic direction. The observations follow closely, but not exactly, the bulk model of  $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$  derived by Takakura et al.

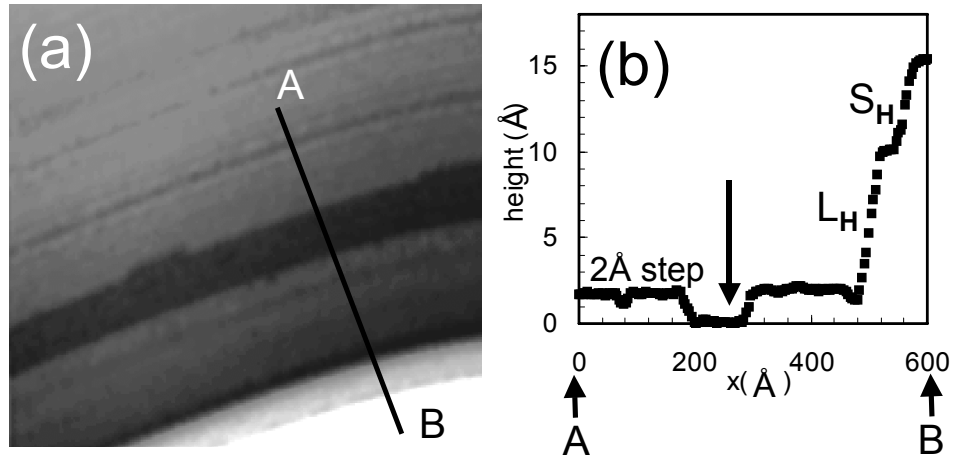
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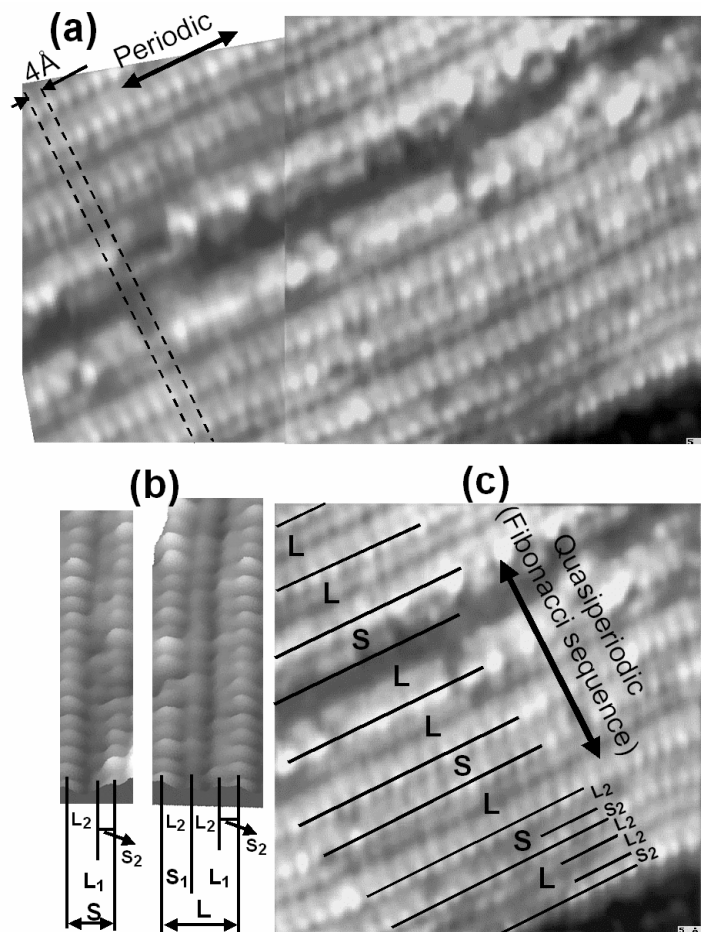
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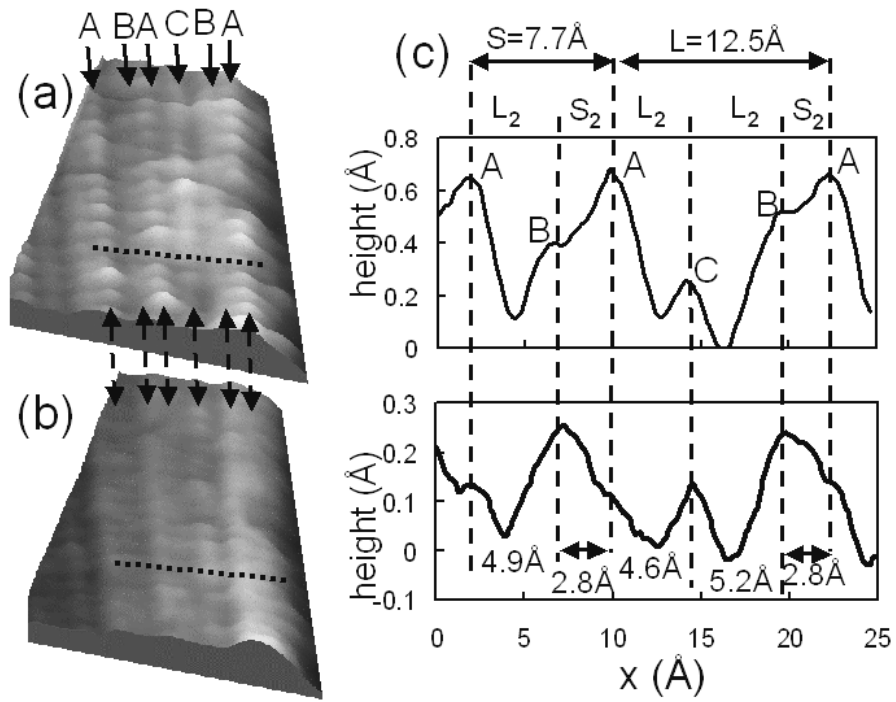




**Figure 1.** (a)  $650 \times 650 \text{ \AA}$  STM image of the 2-fold Al-Ni-Co surface ( $V_s = 1.0\text{V}$ ,  $I_t = 0.1\text{nA}$ ). Steps and terraces composed of rows of atoms are visible. (b) Line profile showing steps with heights  $4.7 \text{ \AA}$  ( $S_H$ ),  $7.8 \text{ \AA}$  ( $L_H$ ), and  $1.9 \text{ \AA}$ . The ratio of  $L_H$  to  $S_H$  is approximately equal to the Golden Mean (1.618), characteristic of aperiodic quasicrystalline structure. The lowest terrace, indicated by the arrow in (b), is a domain where the periodicity along the rows is  $8 \text{ \AA}$ . In the other terraces the periodicity along the rows is  $4 \text{ \AA}$ .



**Figure 2.** (a) Collage of STM images ( $145 \text{ \AA} \times 90 \text{ \AA}$ ) of two contiguous regions in the 2-fold Al-Ni-Co surface. The terraces are made of rows of periodically arranged atoms ( $4 \text{ \AA}$ ) along the ten fold direction and separated by distances L and S. (b) Expanded view showing the interior in the L and S sections. L contains two atomic rows, separated by  $L_2$  and  $S_2$  distances. S contains one row, at distances of  $L_2$  and  $S_2$  from the boundary. (c) The sequence of L and S spacings between rows follows a Fibonacci sequence. The trench in the center of (a) and (c) is due to a missing L+S section. The complete Fibonacci sequence of LSLSLLSLLS is visible in 2a.



**Figure 3.** STM images of the same area acquired at positive and negative bias. (a)  $V_s = +1.2\text{V}$ ,  $I = 0.1\text{nA}$  (b)  $V_s = -1.2\text{V}$ ,  $I = 0.1\text{nA}$ . (c) Line profiles across the dashed lines in (a) and (b) reveal three electronically different atomic rows, labelled A, B, and C.

